

The Iodine Spectrum ©

George Long
Department of Chemistry
Indiana University of Pennsylvania
Indiana, PA 15705
grlong@grove.iup.edu

and

Theresa Julia Zielinski
Department of Chemistry, Medical
Technology, and Physics
Monmouth University
West Long Branch, NJ 07764
tzielins@monmouth.edu

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Prerequisites: This worksheet is appropriate for use in Junior-Senior level physical chemistry classes. To use the document you should have had at least a year of calculus and physics. In addition, it is recommended that you have studied the application of the Schrodinger equation to the harmonic oscillator and rigid rotor. This document is one of a suite of five, the others being the MorsePotential.mcd, BirgeSponer.mcd, FranckCondonBackground.mcd, and FranckCondonComputation.mcd. Each document can be used alone but you will derive the greatest benefits from your studies by using them together. The Mathcad documents in this suite require Mathcad 6.0+.

Goal: The goal of this document is to present a systematic development of the relationship between spectroscopic experiments and the determination of molecular bond lengths in the ground state and electronic excited states for diatomic molecules.

Introduction: Determining the iodine spectrum is a classic experiment in Physical Chemistry. This easily obtained spectrum demonstrates a number of important spectroscopic principles. The study of the experimental spectrum clearly shows the relationship between vibrational and electronic energy levels by introducing the concept of a vibronic transition, demonstrating the anharmonicity of vibrational energy levels; and providing the dissociative limit for the vibronic transitions. With some additional data analysis it is also possible to calculate the parameters for the Morse potential energy function of the excited electronic state, demonstrate the Franck-Condon principle, and compute Franck-Condon factors. This Mathcad document serves as a template for the calculation of the excited state Morse potential curve for iodine from an experimental spectrum. The template could also be used for calculating the excited state Morse potential for any diatomic molecule that has a well defined vibronic spectrum, e.g. Br₂, or CO.

Performance Objectives: After completing the work described in this document you should be able to:

1. calculate the parameters of the Morse potential of a specific electronic state of a diatomic molecule from the appropriate vibronic spectrum of that molecule;
2. explain the concept of anharmonicity, and show how the concept impacts on the calculation;
3. explain the terms Franck-Condon Factor, and Franck-Condon principle, and show where these principles apply in the calculation;
4. predict changes in the appearance of the Morse potential diagram, given changes in the Morse potential function parameters.

Part 1. Preliminaries

In this introduction we examine typical student data obtained from a UV-vis iodine spectrum. This set of data contains 30 peaks listed in the column vector v . These transitions have been identified as emanating from the ground vibronic state of iodine. The analysis of the student data shown here sets the stage for the determination of the spectroscopic properties and equilibrium bond length for the excited state of iodine that the student observed in the spectrum.

$i := 0..29$

$V_i := 47 - i$

$v(v_i) :=$

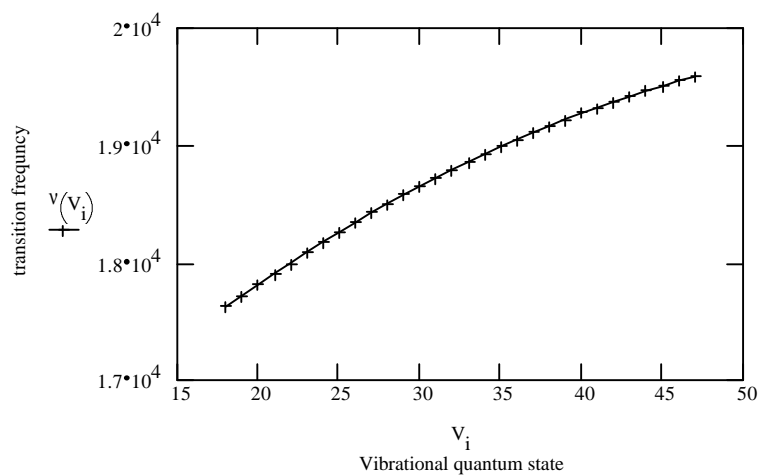
19586.9
19552.3
19504.8
19465.9
19418.3
19375.1
19323.2
19275.7
19223.8
19167.6
19111.4
19050.9
18990.4
18925.6
18860.7
18795.9
18722.4
18653.3
18579.8
18506.3
18428.5
18342.1
18259.9
18177.8
18091.5
17996.3
17909.8
17814.8
17719.7
17624.6

The vibrational quantum numbers for the excited electronic states, V_i , are identified by the array index i . Here we use the fact that the line closest to 542.1 nm (18428 cm^{-1}) is assigned quantum number $V = 27$. (Later we will use v for the vibrational quantum number.) This assignment of quantum number 27 comes from the literature (Sime p 668), and was determined using high resolution spectroscopy that allowed identification of the transitions down to that for the $V=0$ quantum state. All spectral lines are unambiguously labeled relative to this one. The $V=27$ line is not the first line in the list to the left; since it is the 10th we subtract 10 and add 30 to obtain the upper limit, 47 in this case. (Remember, there are 30 items in the list identified by the index i .) **In space to the right ask Mathcad to show the contents of the vectors i , V_i and $47-i$. Verify that in the the vector $47-i$ the 27th entry is associated with the peak at 18428cm^{-1} . Note how the indices vary. What happens to the numbering of the energy levels when we use $47-i$?**

What is the range of vibrational quantum numbers for the frequencies observed in the spectral data given here? What vibrational energy level of the ground state is the origin of each observed transition given here? Hint: consider the state of I_2 in your sample.

Now that the peaks are assigned we can plot frequency versus quantum number. The curvature in the plot shows the anharmonicity of the vibration and it also allows the estimation of the 0 - 0 vibronic transition by extrapolation to $V = 0$. The curvature of the line does not affect the calculation of the Morse potential that will be done later.

Recognizing that the observed vibronic transitions disappear at the dissociation limit, the point where the spectrum becomes continuous, permits us to calculate the dissociation energy D_0 from the vibronic spectrum of a diatomic molecule. We will use a Birge-Sponer plot to do this. We discuss the Birge-Sponer plot in the next section of this document.



Questions for Part 1.

- 1. What would this plot look like if the vibration were harmonic?**
- 2. How accurate do you think your value for the energy of the electronic transition is?**
Hint: calculate a ΔE for the 0-0 transition.

Part 2. The Birge-Sponer Plot

You can calculate the dissociation energy, D_0 , the anharmonicity constant, $\omega_e x_e$, and the vibrational constant, ω_e , from the Birge-Sponer plot. The derivation of the Birge-Sponer equations is available in the companion Mathcad document, BirgeSponer.mcd. For specific definitions of the dissociation energies D_0 , and D_e and other properties of the Morse potential see the companion document MorsePotential.mcd. Additional information can be found in the references at the end of this document especially the papers by Lessinger and McNaught.

In a typical Birge-Sponer plot, you graph the energy difference between the successive spectral bands as a function of the vibrational quantum number of the band plus one, i.e. $v+1$. Notice how indices are used to accomplish this here.

$$i := 46..19$$

We can't include the highest and lowest frequencies because we will be subtracting neighboring pairs of frequencies.

$$q_i := 46 - i$$

q_i is the index that labels the frequency difference vector in ascending order. Check this by displaying the array q_i . The same array index is used for the quantum numbers.

$$v_{(q_i)} := i + 1$$

Mathcad note: we changed the quantum number variable name here. V above on page 2 was an index variable name. Here it is the name of a vector. .

$$\Delta v_{(q_i)} := \frac{1}{2} \cdot (v_{i+1} - v_{i-1}) \cdot \text{cm}^{-1}$$

Compute the difference in the frequency between neighboring vibrational states using Equation 4 from BirgeSponer.mcd.

Check the index, quantum numbers and frequency differences at this point by displaying the various vectors in space at the right. Note how the index change permits plotting of the frequencies in correct order with the correct quantum number. You may need to change the numerical format display precision to show sufficient digits for computation of Δv . Check, by hand, some of the entries of these vectors to be sure you understand how they arise.

$$m1 := \text{slope}(v, \Delta v)$$

$$m1 = -210.409 \cdot \text{m}^{-1}$$

$$\omega_e := \text{intercept}(v, \Delta v)$$

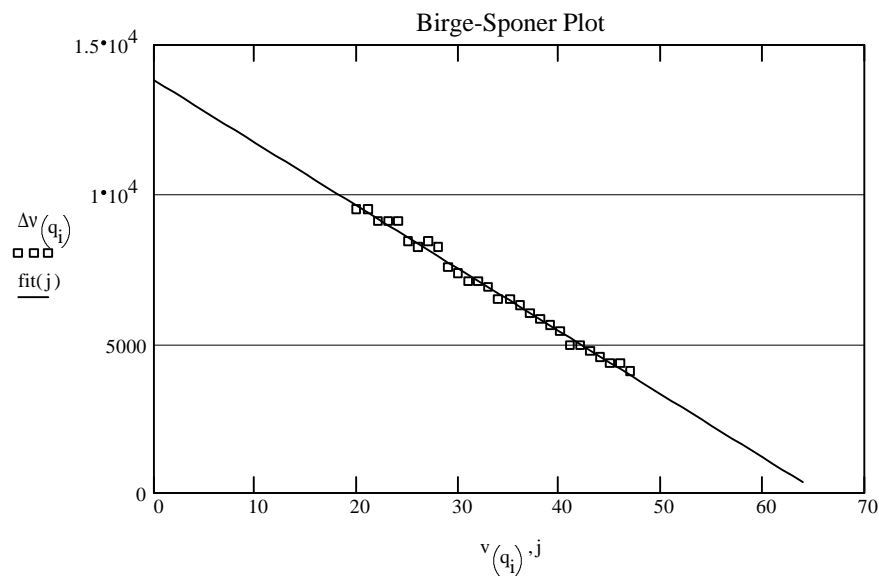
$$\omega_e = 1.383 \cdot 10^4 \cdot \text{m}^{-1}$$

Determine the slope and the intercept of the Birge-Sponer plot. ω_e is the intercept from the Birge-Sponer plot. Notice the use of the slope and intercept functions of Mathcad. The Birge-Sponer plot appears below.

$$j := 0..64$$

$$\text{fit}(j) := (m1 \cdot j + \omega_e)$$

$\text{fit}(j)$ is the straight line using the slope and intercept of the Birge-Sponer plot.



$$\omega_e \chi_e := \left(\frac{-m1}{2} \right)$$

$$\omega_e = 138.253 \cdot \text{cm}^{-1}$$

$$\omega_e \chi_e = 1.052 \cdot \text{cm}^{-1}$$

ω_e is the vibrational constant for the excited state while $\chi_e \omega_e$ is the anharmonicity constant for the excited state.

The x intercept tells you the number of quantum states prior to dissociation as well as the limits for integration used in the calculation of the dissociation energy. **Explain how the x intercept is obtained. This is a good time to go back and look at the BirgeSponer.mcd document again. Here we use equation 3 from BirgeSponer.mcd in the plot above. The Δv of this document was called $\Delta G(v')$ in equation 3 in BirgeSponer.mcd.**

$$\frac{\omega_e}{2 \cdot \omega_e \chi_e} - 1 = 64.707$$

Here we use equation 7 from the BirgeSponer.mcd document to compute v_{max} .

Thus there are 65 quantum states before dissociation.

The area under the Birge-Sponer plot is the dissociation energy, D_0 , of the excited state of the molecule. You can calculate this dissociation energy by integrating the function of the line fit to the data. Here Mathcad does the integration numerically, however, the definite integral of the straight line function can be used instead.

$$D_0 := \int_0^{66} \text{fit}(j) \, dj \quad D_0 = 4.542 \cdot 10^3 \cdot \text{cm}^{-1}$$

$$D_e := \left(D_0 + \frac{\omega_e}{2} \right) \quad D_e = 4.611 \cdot 10^3 \cdot \text{cm}^{-1} \quad \text{Notice that } D_0 \text{ and } D_e \text{ differ by the zero point energy of the excited state.}$$

Questions for Part 2:

1. How do the computed D_0 and D_e values compare to literature values ?
2. What experimental parameters affect the accuracy of the computed dissociation energy values ?
3. How accurate a result is possible using your spectrophotometer ?
4. What type of equipment would you need to determine the dissociation energies more accurately ?

Part 3. Calculation of the Morse potential anharmonicity constant β

The Morse potential is a relatively simple function that is used to model the potential energy of a diatomic molecule as a function of internuclear distance. The Morse potential

$$U(r) := D_e \cdot \left[1 - e^{-\beta \cdot (r - R_e)} \right]^2$$

is defined by three physical constants.

These are D_e , the dissociation energy (not to be confused with D_0), R_e , the equilibrium internuclear distance, and β , the Morse anharmonicity coefficient (not to be confused with the anharmonicity constant $\omega_e x_e$). For more information concerning these constants and their significance see the companion document, MorsePotential.mcd, where hands on practice with the Morse potential will give you a greater appreciation of the function.

First we calculate β , for the excited state of iodine. Start by defining some constants.

Ang := 10^{-10} ·m define the unit for angstroms
c := $2.998 \cdot 10^8$ ·m·sec⁻¹ the speed of light
 π = 3.142 note that π is predefined by Mathcad
h := $6.6261 \cdot 10^{-34}$ ·joule·sec Planck's constant
 μ := $1.053 \cdot 10^{-25}$ ·kg the reduced mass of iodine

Calculate β using the following equation. Notice how Mathcad made the proper unit conversions. When you do the calculation by hand it is important to note that all quantities must be in SI units (kg, m, sec, joules). The cm⁻¹ is not an SI unit.

$$\beta := \sqrt{\frac{2 \cdot \pi^2 \cdot \mu \cdot c}{D_e \cdot h}} \cdot \omega_e$$

$\beta = 1.974 \cdot 10^{10} \cdot \text{m}^{-1}$

Exercise: Have Mathcad display cm⁻¹ as the units for β .

Questions for Part 3:

1. From where does the equation for β come?
Derive this equation from the Morse potential.
2. With what property of a bond is β associated?
3. Verify that the unit for β is m⁻¹.

Part 4. Calculating the internuclear distance (R_e) of the excited state.

To calculate R_e for the excited state of I_2 we need two more pieces of data. First, we need the frequency of the maximum absorbance of the spectrum, and we need the equilibrium bond length, R_e , for the ground state. The frequency with the maximum absorbance can be determined from the spectrum. Although R_e can be obtained from the fluorescence spectrum, it is usually given to students for the data analysis in the typical iodine experiment conducted in most physical chemistry undergraduate laboratories.

$A_{\max} := 18860.7 \cdot \text{cm}^{-1}$ Frequency of the maximum absorbance from inspection of the spectrum.

$T_e := 15300 \cdot \text{cm}^{-1}$ Frequency of the 0 - 0 or ground state to ground state transition determined from the data or obtained from the literature.

$R_1 := 2.66 \cdot 10^{-10} \cdot \text{m}$ the equilibrium bond length for the ground state as found in the literature

From the Franck-Condon principle, we know that the maximum absorbance will take place where there is the greatest overlap between an upper state wave function with vibrational quantum number v' and ground state vibrational wave function with quantum number $v''=0$. The magnitude of the overlap is given by the Franck-Condon factors (see the companion documents FranckCondonBackground.mcd and FranckCondonComputation.mcd for an in depth introduction to Franck-Condon factors). At the maximum absorbance the value of r in the excited state equals R_1 , the equilibrium bond length of the ground state. So, if we know the energy of this transition, we can use the Morse potential equation to solve for the equilibrium bond length (R_e in the notation used here) of the excited state. The Morse potential energy function is:

$$U(r) := T_e + D_e \cdot \left[1 - e^{-\beta \cdot (r - R_e)} \right]^2$$

Substitute R_1 for the bond length of the excited state at the moment of the electronic transition, i.e. $R_1 = r$, and A_{\max} for $U(r)$. When you do this you get:

$$A_{\max} = T_e + D_e \cdot \left[1 - e^{-\beta \cdot (R_1 - R_e)} \right]^2$$

Rearrange the equation to solve for R_e . The result is:

$$R_e := R_1 + \frac{1}{\beta} \cdot \ln \left(1 + \sqrt{\frac{A_{\max} - T_e}{D_e}} \right)$$

The solution actually has 2 roots. The larger root is chosen because R_e , the bond length in the excited state, must be greater than R_1 , the bond length of the ground state, for iodine.

$$R_e = 2.979 \cdot 10^{-10} \cdot \text{m}$$

Question: What spectroscopic observation would tell us which root to choose in the calculation here?

Exercise: Use Morse potential diagrams to illustrate Franck-Condon Factors, and explain the appearance of a maximum absorbance.

Question: What are the units of A_{max}? Is this an energy unit?

Finally, we can plot the Morse potentials of both the ground (X) state and the (B) excited state potentials in one figure. The plot below shows both.

```
i := 0..500 }
ri := (.5 + i·.01)·Ang } this defines the values of r in terms of the array index, i
}
```

```
groundDe := 4398·cm-1 }
βg :=  $\frac{1.873}{\text{Ang}}$  Rge := 2.66·Ang } ground state parameters, from the literature
}
```

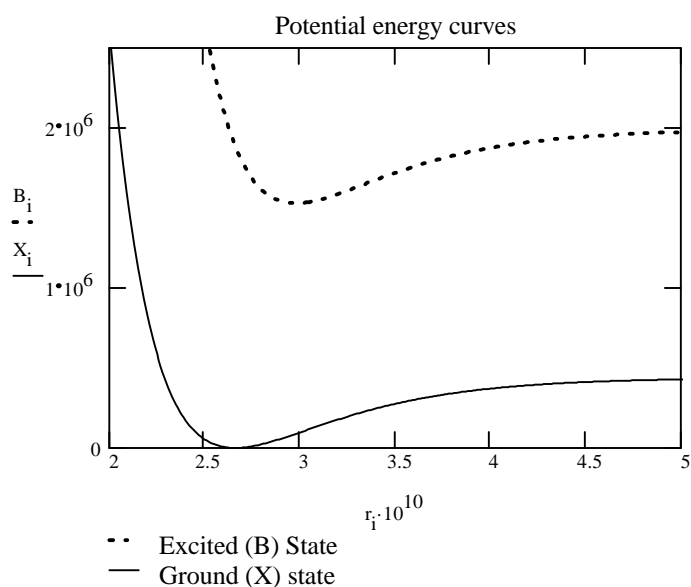
Now calculate the potential energy using the Morse potential function.

Excited "B" State

Ground "X" State

$$B_i := \text{De} \cdot \left[1 - e^{-\beta \cdot (r_i - R_e)} \right]^2 + T_e$$

$$X_i := \text{groundDe} \cdot \left[1 - e^{-\beta_g \cdot (r_i - R_{g_e})} \right]^2$$



General Questions.

1. Vary the value of the β in the Morse potential equation. How does the value of β affect the shape of the Morse potential? Do the same for R_e and D_e . Record your observations in your notebook.
2. Will obtaining a different frequency for the maximum absorbance make a big difference in the computed parameters? Change your value for A_{max} and report what happens to the computed Morse parameters. Explain your results.
3. Under what conditions would you obtain a different A_{max} value? Why?
3. Does any other one datum make a significant difference in the calculations? Discuss the accuracy of your results based on the computational manipulations performed in this document.

Mastery Exercise:

Obtain the UV-vis spectrum for some other diatomic molecule. Use this document as a template for constructing the data analysis for the molecule. Compare and contrast the spectroscopic properties of the iodine molecule to the other molecule you chose. Discuss the differences between the molecules with respect to their chemical and physical properties.

Acknowledgment:

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References:

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3. D'alterio, R, Mattson, R., Harris, R., "Potential Curves for the I_2 Molecule: An Undergraduate Physical Chemistry Experiment", *J. Chem. Educ.* 1974, 51, 282-284.
4. Lessinger, L., "Morse Oscillators, Birge-Sponer Extrapolation, and the Electronic Absorption Spectrum of I_2 ", *J. Chem. Educ.* 1994, 71, 388-391.
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6. Verma, R. D., "Ultraviolet Spectrum of the Iodine Molecule", *J. Chem. Phys.* 1960, 32, 738-749. (this paper gives an excellent set of data for Iodine and a good figure (Figure 9) for the ground state potential energy function compared to the Morse potential. The inadequacy of the Morse potential at larger interatomic separations is clear. The failure of the Morse potential at internuclear separations one Angstrom greater than the equilibrium bond length is attributed to London forces. These are more commonly called van der Waals forces and they follow a $1/r^6$ function rather than the exponential function given by the Morse potential.)